

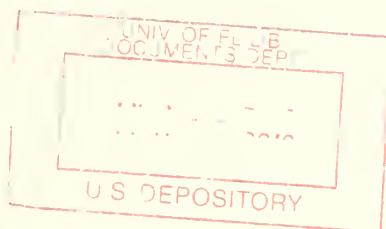
DETERMINATION OF NICKEL AND COPPER CHROMATES  
AND NICKEL, COPPER, AND MAGNESIUM ARSENATES  
IN TREATED WOOD

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DETERMINATION OF NICKEL AND COPPER CHROMATES AND NICKEL,  
COPPER, AND MAGNESIUM ARSENATES IN TREATED WOOD

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The methods to be described were required for a study of wood treated with different combinations of salts. They will be recognized in their separate parts as common procedures of chemical analysis with some minor changes which were found to be necessary. Preference has been given to methods requiring apparatus commonly available and also to volumetric methods as being more suitable than gravimetric methods for routine analyses.

Destruction of Organic Material

The destruction of organic matter by a mixture of sulfuric, nitric, and perchloric acids was found satisfactory in the determination of any of the ions present separately or in combination. The procedure used is as follows:

To a 5-gram sample of sawdust in a Kjeldahl flask add 40 ml. of concentrated nitric acid, 15 ml. of G.F.S. oxidant (2 parts 80 percent sulfuric acid to 1 part 70 percent perchloric acid by volume) and a few glass beads. Heat slowly at first, then with a medium flame until all the nitric and most of the perchloric acid have boiled off, leaving the inorganic salts in a clear, sulfuric-acid solution. If the sample contains chromium, add an additional 5 ml. of 70 percent perchloric acid at the start of the digestion. Prolonged boiling at the end should be avoided as it causes the formation of chromic ion which precipitates as chromic sulfate and is hard to redissolve.

In the determination of heavy metals and chromium, but not arsenic, dry ashing may be used. It requires less attention than the acid digestion, but does not yield results in so short a period of time and with some combinations an occasional sample yields an ash that is difficult to dissolve. The sample is ashed at 550° C. After cooling, the ash is taken up with 10 ml. of dilute sulfuric acid (1:1), and if chromium is present, 2.5 ml. of 70 percent perchloric acid is added and the solution heated until it turns orange.

Copper and Chromium

The electrolytic deposition of copper leaving chromium in solution in reduced form is the most convenient separation. Should the necessary

equipment be unavailable, copper may be separated from chromium by the Haen-Low method and determined iodometrically. Chromium in the remaining solution is determined iodometrically. Average recoveries of known amounts were 99.7 percent for copper and 99.2 percent for chromium. The procedure is as follows:

Transfer the digestion solution to a beaker and dilute to 100 ml., add two 1-inch squares of sheet aluminum, cover the beaker with a watch glass and keep the solution just below boiling for 15 minutes when the copper will be deposited on the aluminum. Filter and wash by decantation, keeping as much of the copper as possible in the beaker. Collect the filtrate and washings in a 500 ml. glass-stoppered, Erlenmeyer flask and save for the determination of chromium. Dissolve the copper in the beaker by warming it with 6 ml. of dilute nitric acid (1:1). Pour this acid solution of copper over the filter paper to dissolve any copper which may have been retained, collecting the solution in an Erlenmeyer flask. Wash beaker and filter with hot water.

### Copper

Add 5 ml. of bromine water to the acidic copper solution and boil until the solution is again blue and no more bromine remains (starch-iodide paper test). Make the solution ammoniacal by the careful addition of ammonium hydroxide, then remove the excess ammonia by boiling. Adjust the volume of the solution to 50 ml., add 6 ml. glacial acetic acid, cool, and add 3 grams of potassium iodide. Titrate the liberated iodine with sodium thiosulfate, using starch indicator. 1cc. N/10  $\text{Na}_2\text{S}_2\text{O}_3$  = 0.01596 gm.  $\text{CuSO}_4$  = 0.006357 gm. Cu.

### Chromium

Make the filtrate from the copper separation alkaline with sufficient sodium hydroxide to dissolve the aluminum hydroxide which first forms. Add an excess of bromine water and boil after which the solution should be yellow and clear. A greenish color indicates chromic ion and the need of more bromine water. A precipitate indicates ferric hydroxide which must be removed by filtration. Acidify the solution with sufficient sulfuric acid to dissolve the aluminum hydroxide which first forms. Add 20 ml. of 30 percent sodium bisulfate and boil to expel bromine. Adjust the volume to about 150 ml., cool, add 10 ml. of concentrated hydrochloric acid and 3 grams of potassium iodide. After allowing the stoppered flask to stand 5 minutes, dilute and titrate with sodium thiosulfate, using starch indicator. 1 ml. N/10  $\text{Na}_2\text{S}_2\text{O}_3$  = 0.0054 gm.  $\text{Na}_2\text{CrO}_4$  = 0.001734 gm. Cr.

### Copper and Arsenic

Copper and arsenic are separated by precipitating magnesium ammonium arsenate from an ammoniacal solution in which copper is soluble. Both

copper and arsenic are then determined iodometrically. Average recoveries of known amounts were 100.1 percent for copper and 99.0 for arsenic. The procedure is as follows:

Transfer the digestion solution to an Erlenmeyer flask and dilute to about 75 ml. For each 0.1 gram of arsenic add 10 ml. of magnesia mixture (66.4 gm.  $MgSO_4 \cdot 6H_2O$ , 86.4 gm.  $(NH_4)_2SO_4$ , 5 ml.  $H_2SO_4$  diluted to 1 liter). Neutralize with ammonium hydroxide and add an excess equal to one-third the volume of the neutral solution. Allow the solution to stand for 12 hours, then filter and wash by decantation with 1.5 N ammonium hydroxide, keeping most of the precipitate in the flask. Save the filtrate and washings for the determination of copper.

### Arsenic

Dissolve the precipitate on the filter with 20 ml. dilute sulfuric acid (1:3) and collect in the flask in which the precipitation was made originally. Wash the filter with hot water and dilute to 250 ml. Add 2 grams of potassium iodide and boil to a volume of 50 ml. Add starch solution and decolorize with a minimum of sodium thiosulfate solution. Neutralize to litmus with sodium hydroxide, then make just acid with a few drops of sulfuric acid. Neutralize with sodium bicarbonate, cool, and add an excess of 5 grams of the latter. Dilute to about 250 ml. and titrate with N/10 iodine solution. 1 cc. N/10  $I_2$  = 0.0093 gm.  $Na_2HAsO_4$  = 0.00375 gm. As.

### Copper

Proceed as above under "Copper," omitting the treatment with bromine.

### Nickel and Chromium

The determination of nickel and chromium does not require their separation. Chromium may be determined iodometrically in the presence of nickel. Nickel in wood, either alone or in the presence of chromium or arsenic, may be determined accurately by precipitation from the acid digestion solution with dimethyl glyoxime. However, for a large number of samples the titration of nickel with potassium cyanide is more rapid. Chromium in chromic state interferes with this titration and must be oxidized to chromate. Average recoveries of known amounts were from 99.5 for nickel and 100.2 for chromium. The procedure is as follows:

### Chromium

Dilute the acid digestion mixture to 1 liter. Take a 100 ml. aliquot. Precipitate any iron present with ammonium hydroxide, adding sufficient excess to redissolve nickel hydroxide. Filter, if necessary, and determine chromate iodometrically as outlined above.

## Nickel

Take a 100 ml. aliquot, make slightly ammoniacal, and dilute to about 250 ml. Tartaric acid may be added to dissolve any precipitated ferric hydroxide. Make the solution slightly acid with hydrochloric acid and add exactly 5 ml. of 0.1 percent silver nitrate solution. Dissolve the precipitate of silver chloride with a minimum of ammonium hydroxide. Add 10 ml. of 1.6 percent potassium iodide solution which forms a precipitate of silver iodide. Titrate with a standardized solution of potassium cyanide (4.6 gm. KCN and 1.7 gm. NaOH per liter) until the precipitate of silver iodide has just dissolved, leaving a clear solution. Note the titration and determine the blank to correct for the amount of potassium cyanide used to dissolve the silver iodide indicator. This is done by adding an additional 10 ml. of potassium iodide solution and 5 ml. of silver nitrate solution and titrating until the precipitate has again dissolved. Repeat and subtract the average blank from the original titration. Standardize the potassium cyanide solution against a solution of nickel sulfate which has been assayed by the precipitation of nickel with dimethyl glyoxime.

## Nickel and Arsenic

The determination of nickel and arsenic, like nickel and chromium, does not involve a separation of the elements. The arsenic in the acid digestion mixture is reduced with potassium iodide and titrated with iodine after which the solution is titrated with potassium cyanide to determine nickel. Average recoveries of known amounts were 99.6 percent for nickel and 99.0 percent for arsenic.

## Magnesium and Arsenic

In the acid digestion solution containing both magnesium and arsenic, the latter is first determined by reduction with potassium iodide and titration with iodine. Magnesium is then determined in the same solution by precipitating magnesium ammonium arsenate, filtering, dissolving the precipitate with acid, reducing the arsenic with potassium iodide and titrating with iodine. Magnesium is then calculated from the arsenic. This is a modification of a method described by Meade<sup>1</sup> who titrated the iodine liberated by the acid solution of magnesium ammonium arsenate. More accurate results were obtained than by the use of Meade's original procedure. This was ascribed to the difficulty of controlling the quantitative liberation of iodine by arsenate. Average recoveries of known amounts were 100.4 percent for magnesium. The procedure is as follows:

<sup>1</sup>Jour. Amer. Chem. Soc. 21:746 (1899).

Magnesium

Acidify the solution which remains from the titration of arsenic with sulfuric acid. Boil to a volume of about 75 ml. and add 25 ml. of 10 percent disodium arsenate. Add a suitable excess of ammonia to precipitate magnesium ammonium arsenate and proceed as under the determination of arsenic in the presence of copper. 1 ml. N/10  $I_2$  = 0.00602 gm.  $MgSO_4$  = 0.001216 gm. Mg.

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